



⑫

## EUROPEAN PATENT APPLICATION

⑬ Application number: 84301072.9

⑮ Int. Cl. 3: C 07 C 121/60, C 07 C 121/75,  
C 07 C 120/00, C 07 C 49/813,  
C 07 C 49/84, C 07 C 45/46,  
C 09 K 3/34

⑭ Date of filing: 20.02.84

⑩ Priority: 18.02.83 JP 25689/83  
15.03.83 JP 42992/83  
28.03.83 JP 52179/83  
18.04.83 JP 68188/83

⑯ Applicant: Chisso Corporation, 6-32,  
Nakanoshima 3-chome Kita-ku, Osaka-shi Osaka-fu (JP)

⑭ Date of publication of application: 26.09.84  
Bulletin 84/39

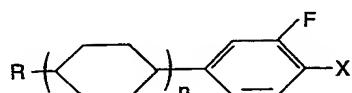
⑰ Inventor: Sugimori, Shigeru, 2493-10, Fujisawa,  
Fujisawashi Kanagawaken (JP)  
Inventor: Kojima, Tetsuhiko, 10-3, Otsutomocho  
Kanazawaku, Yokohamashi Kanagawaken (JP)  
Inventor: Goto, Yasuyuki, 10-3 Otsutomocho  
Kanazawaku, Yokohamashi Kanagawaken (JP)  
Inventor: Isayama, Toyoshiro, 10-3, Otsutomocho  
Kanazawaku, Yokohamashi Kanagawaken (JP)  
Inventor: Nigorikawa, Kazunori, 10-3, Otsutomocho  
Kanazawaku, Yokohamashi Kanagawaken (JP)

⑯ Designated Contracting States: CH DE GB LI

⑯ Representative: Ruffles, Graham Keith et al, MARKS &  
CLERK 57-60 Lincoln's Inn Fields, London WC2A 3LS  
(GB)

⑭ Fluorobenzene derivatives and liquid crystal compositions containing the same.

⑭ Fluorobenzene derivatives expressed by the general formula



wherein n represents 1 or 2, X represents CN or COCH<sub>3</sub>, and R represents a hydrogen atom or an alkyl or alkoxy group each of 1 to 15 carbon atoms are liquid crystal compounds having a large positive dielectric anisotropy value and also a low viscosity and a good stability to heat, light, air and water, and are suited for use in liquid crystal compositions.

EP 0 119 756 A1

FLUOROBENZENE DERIVATIVES AND LIQUID CRYSTAL  
COMPOSITIONS CONTAINING THE SAME

This invention relates to novel liquid crystal compounds having a positive dielectric anisotropy, and liquid 5 crystal compositions containing the same.

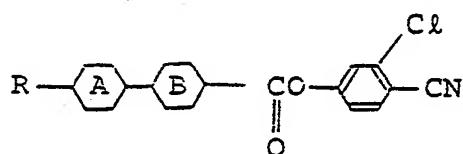
Liquid crystal display elements utilize the optical anisotropy and dielectric anisotropy of liquid crystal substances, and are classified into various types such as TN (twisted nematic) type, DS (dynamic scattering) 10 type, guest-host type, DAP type, White-Tailor type, etc according to their display modes. The properties required of the liquid crystal substances for their respective uses are different. For example, liquid crystal substances having a positive dielectric 15 anisotropy  $\Delta\epsilon$  might be required or one having a negative one are required or one having an intermediate value, depending on the kind of display elements. Anyhow, however, in any mode, the liquid crystal substances have to exhibit a liquid crystal phase in temperature ranges 20 as broad as possible, around room temperature, and also have to be stable to heat, air, light, etc. At present, however, there is no single compound which alone satisfies all such conditions. It is the present state of the art that several kinds of liquid crystal

compounds or such compounds and non-liquid crystalline compounds are mixed to obtain a mix which will meet current practical uses.

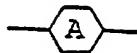
Recently, the need particularly for liquid crystal  
5 display elements which can be driven at low voltages has increased, and in order to satisfy such a requirement, liquid crystal compositions having a larger  $\Delta\epsilon$  value are usually required.

In general, liquid crystal compositions having a desired  
10  $\Delta\epsilon$  value can be obtained by adequately mixing compounds having a positive  $\Delta\epsilon$  value with those having a negative  $\Delta\epsilon$  value. Thus, in order to obtain a liquid crystal composition having a large positive  $\Delta\epsilon$  value, a component having as large a positive  $\Delta\epsilon$  value as  
15 possible will have to be used. In this case, however, the component will still have to have a good compatibility with other components and extend the mesomorphic range of the resulting composition or at least not narrow it.

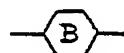
In order to satisfy such an object, we have described in  
Japanese patent application laid-open No Sho  
57-154158/1982 a series of carboxylic acid  
3-chloro-4-cyanophenyl esters expressed by the general  
5 formula



wherein R' represents an alkyl group or alkoxy group of  
1 to 10 carbon atoms and



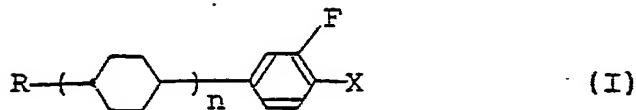
10 and



represents a benzene or cyclohexane ring.

Liquid crystal display elements having a higher level of  
performances continue to be needed, and compounds having  
15 a lower viscosity and a good stability to heat, light,  
air and moisture have been required. The present  
invention has been made to meet such a demand.

The present invention resides in fluororobenzene derivatives expressed by the general formula



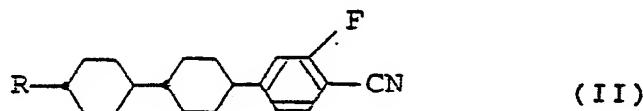
5 wherein n represents 1 or 2; X represents CN or COCH<sub>3</sub>; and R represents hydrogen or an alkyl or alkoxy group of 1 to 15 carbon atoms. The present invention also provides liquid crystal compositions containing the compounds.

10 In particular, compounds of the above general formula wherein X represents CN have a positive dielectric anisotropy value typically as large as about +30, a low viscosity for such a value and a good stability to heat, light, air and water and exhibit a liquid crystal phase in broad temperature range; hence they are suitable as 15 components constituting a liquid crystal composition which has a large  $\Delta\epsilon$  value, a low viscosity and a broad mesomorphic range.

More particularly, compounds of the general formula wherein X represents CN and n is 2, that is,

3-fluoro-4-cyano-1-[trans-4-(trans-4-substituted cyclohexyl)cyclohexyl]benzenes expressed by the general

5 formula



wherein R is as defined above, exhibit a liquid crystal phase within a broad mesomorphic range up to high temperatures. Furthermore, compounds of the formula (I)

10 wherein X represents  $\text{COCH}_3$  have a low viscosity although their  $\Delta\epsilon$  values are small. Particularly, compounds of the formula (I) wherein X represents  $\text{COCH}_3$  and n is 2 exhibit a liquid crystal phase in a broad temperature range. Such compounds of the formula 15 (I) wherein X represents  $\text{COCH}_3$  can be obtained as intermediate compounds in the preparation of compounds of the formula (I) wherein X represents CN.

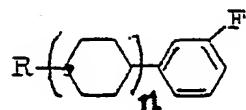
The present invention also provides a process for preparing the compounds of formula (I). In the process, 20 a 1-fluoro-3-(4-substituted cyclohexyl)benzene corresponding to a compound of formula (I) which has hydrogen in place of the substituent X, is acetylated to

give a compound of formula (I) where X is  $\text{COCH}_3$ , and the  $\text{COCH}_3$  group is optionally converted to a nitrile group.

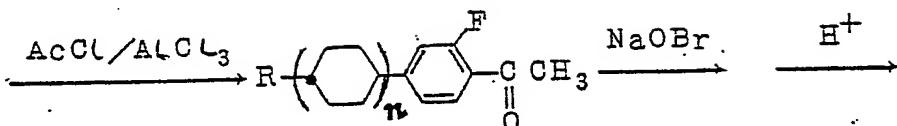
Aspects of the process will now be described in more 5 detail, referring to the following reaction scheme:

A 1-fluoro-3-(4-substituted cyclohexyl)benzene (a compound of the formula (2) wherein n is 1) or a 1-fluoro-3-[trans-4-(trans-4-substituted cyclohexyl)-cyclohexyl]benzene (a compound of the formula (2) 10 wherein n is 2), can be prepared according to a known method (for example, the method described in USP 4405488), and is preferably reacted with acetyl chloride in the presence of aluminium chloride using  $\text{CS}_2$  as solvent to obtain a 2-fluoroacetophenone derivative (3) 15 corresponding to the formulae (IV) and (V) of the claimed compounds. This derivative can then be reacted for instance with sodium hypobromite in dioxane to obtain a carboxylic acid compound (4) which may be reacted with thionyl chloride in toluene to obtain an 20 acid chloride compound, which in turn may then be reacted with aqueous ammonia to obtain an acid amide compound (5) and then dehydrated with thionyl chloride to obtain the desired 3-fluoro-4-cyano-1-(trans-4-substituted cyclohexyl)benzene (III) or 25 3-fluoro-4-cyano-1-[trans-4'-(trans-4-substituted cyclohexyl)cyclohexyl]benzene (II).

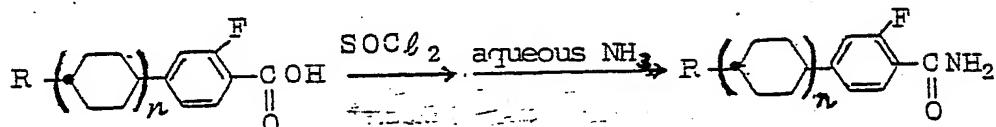
The foregoing is illustrated by the following chemical formulas:



(2)

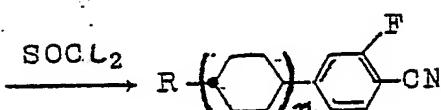
 $\xrightarrow{\text{NaOBr}}$  $\xrightarrow{\text{H}^+}$ 

(3), (IV, V)



(4)

(5)



(II, III)

The present invention will be further described in detail by way of Examples.

#### Example 1

Preparation of 2-fluoro-4-(trans-4-heptylcyclohexyl)-acetophenone (a compound of the formula (I) wherein X represents  $\text{COCH}_3$  and n is 1, i.e. a compound of the formula (V) wherein R represents  $\text{C}_7\text{H}_{15}$ ).

1-Fluoro-3-(4-heptylcyclohexyl)benzene (18 g) was dissolved in  $\text{CS}_2$  (50 ml), and aluminum chloride (7.2 g) was then dissolved in the solution, followed by adding acetyl chloride (5.3 g) with stirring at 2 to 5°C for 5 10 minutes, gradually raising the temperature up to 35°C, keeping this temperature for 2 hours, cooling the mixture, adding 6N hydrochloric acid (50 ml), subjecting the resulting oil layer to extraction with toluene (100 ml), washing the solution with water till 10 the washing liquid became neutral, distilling off the solvent under reduced pressure and recrystallizing the residue from ethanol to obtain the objective 2-fluoro-4-(trans-4-heptylcyclohexyl)acetophenone (yield: 9 g). This product was of a monotropic liquid crystal and exhibited a melting point (C-I point) of 35.6 ~ 40.2°C and a nematic-clearing point (N-I point) of 21.5°C.

The following compounds were prepared in the same manner as above:

20 2-fluoro-4-(trans-4-propylcyclohexyl)acetophenone  
m.p. 63.3 ~ 64.7°C

2-fluoro-4-(trans-4-butylcyclohexyl)acetophenone  
m.p. 73 ~ 77°C

2-fluoro-4-(trans-4-pentylcyclohexyl)acetophenone  
m.p. 10.1 ~ 13.5°C

2-fluoro-4-(trans-4-hexylcyclohexyl)acetophenone

m.p. 58.2 ~ 62.2°C

N—I point 12.9°C

Example 2

Preparation of

5 1-cyano-2-fluoro-4-(trans-4-heptylcyclohexyl)-  
benzene (a compound of the formula (I) wherein X  
represents CN and n is 1, i.e. a compound of the  
formula (III) wherein R represents C<sub>7</sub>H<sub>15</sub>)

10 Crystals of 2-fluoro-4-(trans-4-heptylcyclohexyl)-  
acetophenone obtained in Example 1 (15 g) were dissolved  
in dioxane (50 ml) and cooled down to 10°C or lower.  
Separately, sodium hydroxide (40 g) was dissolved in  
ice water (200 ml), and bromine (40 g) was dropwise added  
to the solution to obtain a solution of sodium hypo-  
15 bromite. This solution was dropwise added with stirring  
to the solution of the above compound, while keeping  
the temperature at 10°C or lower, warming the mixture  
to 35°C over 3 hours, allowing to stand overnight, adding  
6N-hydrochloric acid (100 ml) for acidification, filtering  
20 the mixture to recover the precipitate and recrystallizing  
it from acetic acid (20 ml) to obtain crystals of 2-  
fluoro-4-(trans-4-heptylcyclohexyl)benzoic acid (4).

Crystals of this compound (4) (12 g) were suspended  
in toluene (20 ml), followed by adding thionyl chloride  
25 (5.9 g) to the suspension, reacting them at 70°C for

6 hours, distilling off excess thionyl chloride under reduced pressure, pouring a residual oily substance in an aqueous ammonia (50 ml), recovering the resulting precipitate by filtration, and recrystallizing it

5 from toluene to obtain crystals of 2-fluoro-4-(trans-4-heptylcyclohexyl)benzoic acid amide (5). The crystals (1.5 g) were dissolved in a mixture of toluene (50 ml) with dimethylformamide (50 ml), followed by adding thionyl chloride (5 g), subjecting

10 the mixture to dehydration reaction at 80°C for 5 hours, cooling the resulting material, adding ice water (50 ml), subjecting it to extraction with toluene (200 ml), distilling off the resulting oily substance under reduced pressure, filtering off

15 insoluble matters, putting the filtrate in a refrigerator for crystallization, and recrystallizing the resulting crystals from n-heptane to obtain crystals of 1-cyano-2-fluoro-4-(trans-4-heptylcyclohexyl)benzene (yield: 0.2 g). The crystals

20 exhibited a C-N point of 19.6 ~ 20.9°C and a N-I point of 21.2°C.

Compounds of the formula (III) containing other substituents were obtained in the same manner as above.

Example 3

Preparation of 4-[trans-4-(trans-4-propylcyclohexyl)cyclohexyl]-2-fluoroacetophenone  
(a compound of the formula (I) wherein X  
5 represents  $\text{COCH}_3$  and n is 2, i.e. a compound  
of the formula (IV) wherein R represents  $\text{C}_3\text{H}_7$   
10 3-[Trans-4-(trans-4-propylcyclohexyl)cyclohexyl]fluorobenzene (5 g) was dissolved in  $\text{CS}_2$   
(50 ml), followed by adding aluminum chloride (4 g),  
dropwise adding acetyl chloride (3 g) with stirring  
15 at 5°C or lower, raising the temperature up to 35°C,  
agitating the mixture for 2 hours, adding cold  
hydrochloric acid, subjecting the resulting  
precipitate to filtration and washing with ice water,  
and recrystallizing it from a mixed solvent of acetone  
20 with toluene to obtain the objective 4-[trans-4-(trans-  
4-propylcyclohexyl)cyclohexyl]-2-fluoroacetophenone  
(yield: 18%). It exhibited a C-N point of 88 ~ 90°C  
and a N-I point of 293°C.  
25 4-[Trans-4-(trans-4-butylcyclohexyl)cyclohexyl]-  
2-fluoroacetophenone was obtained in the same manner  
as above. It exhibited a C-N point of 50 ~ 53.5°C  
and a N-I point of 123°C.

Example 4

Preparation of 3-fluoro-4-cyano-1-[trans-4-(trans-4-propylcyclohexyl)cyclohexyl]benzene  
(a compound of the formula (I) wherein X  
5 represents CN and n is 2, i.e. a compound of  
the formula (II) wherein R represents  $C_3H_7$ )  
4-[Trans-4-(trans-4-propylcyclohexyl)cyclohexyl]-  
2-fluoroacetophenone (0.7 g) was suspended in dioxane  
(50 ml), followed by keeping the suspension at 10°C  
10 or lower, dropwise adding to it with stirring,  
a solution of sodium hypobromite prepared by adding  
bromine (1.6 g) to sodium hydroxide (2 g) and ice  
water (30 ml), raising the temperature up to 35°C,  
continuing agitation for 5 hours, cooling the resulting  
15 material, acidifying it with 6N-hydrochloric acid, and  
subjecting the precipitate to filtration and water-  
washing to obtain 4-[trans-4-(trans-4-propylcyclohexyl)-  
cyclohexyl]-2-fluorobenzoic acid, which was then  
recrystallized from acetic acid and dried. The  
20 product (0.6 g) was dissolved in toluene (20 ml),  
followed by adding thionyl chloride (2 g), refluxing  
the mixture for 3 hours, distilling off excess  
thionyl chloride under reduced pressure, pouring  
the resulting residual oily substance in an aqueous  
25 ammonia, filtering and water-washing the resulting

precipitate, and recrystallizing it from toluene to obtain 4-[trans-4-(trans-4-propylcyclohexyl)-cyclohexyl]-2-fluorobenzoic acid amide. This product (0.4 g) was dissolved in dimethylformamide (10 ml) and toluene (10 ml), followed by adding thionyl chloride (2 g), refluxing the mixture for 4 hours, cooling it, adding cold water, subjecting the mixture to separation and extraction with toluene (50 ml), water-washing the resulting oily layer till the washing liquid became neutral, distilling off toluene under reduced pressure, and recrystallizing a remaining oily substance from a mixed solvent of toluene with acetone to obtain crystals of the objective 3-fluoro-4-cyano-1-[trans-4-propylcyclohexyl)cyclohexyl]benzene (yield: 0.1 g). This product exhibited a crystalline-smectic point of 53.8°C; a smectic-nematic point of 89.8°C and a nematic-clearing point of 207°C.

3-Fluoro-4-cyano-1-[trans-4-(trans-4-substituted cyclohexyl)cyclohexyl]benzenes having other substituents were obtained in the same manner as above.

Use example 1

A liquid crystal composition (A) consisting of trans-4-propyl-(4'-cyanophenyl)cyclohexane 24% by weight, trans-4-pentyl-(4'-cyanophenyl)cyclohexane 36% by weight,

trans-4-heptyl-(4'-cyanophenyl)cyclohexane

25% by weight, and

trans-4-pentyl-(4"-cyanobiphenyl)cyclohexane

15% by weight,

5 had a nematic temperature range of -10°C ~ +72.1°C and a viscosity at 20°C of 28 cp. When the composition was sealed in a TN cell having a transparent electrode and a distance between the inner walls, of 10  $\mu$ m, the cell exhibited a threshold voltage of 1.76 V and  
10 a saturation voltage of 2.40 V.

2-Fluoro-4-(trans-4-heptylcyclohexyl)acetophenone of Example 1 (5 parts by weight) was added to the above liquid crystal composition (A) (95 parts by weight). The resulting liquid crystal composition  
15 had a N-I point of 68.4°C, but its viscosity at 20°C was 27 cp and when it was sealed in the above TN cell, the threshold voltage and the saturation voltage were 1.69 V and 2.32 V, respectively.

Use example 2

20 A liquid crystal composition consisting of the above liquid crystal composition (A) (90% by weight) and 1-cyano-2-fluoro-4-(trans-4-heptylcyclohexyl)-benzene of Example 2 (10% by weight) had a N-I point of 66.3°C, a viscosity at 20°C of 27 cp and a  $\Delta\epsilon$  of 13.4, and  
25 when it was sealed in the above cell, the threshold voltage

and the saturation voltage were 1.62 V and 2.24 V, respectively.

Use example 3

A liquid crystal composition (B) consisting of  
5 trans-4-propyl-(4'-cyanophenyl)cyclohexane  
28 by weight,

### trans-4-pentyl-(4'-cyanophenyl)cyclohexane

42% by weight and

### trans-4-heptyl-(4'-cyanophenyl)cyclohexane

10 30% by weight,

exhibited a nematic temperature range of  $-3^{\circ}\text{C}$  ~  $+52^{\circ}\text{C}$ .

The threshold voltage, the saturation voltage and the viscosity at 20°C were 1.6 V, 2.2 V and 23 cp respectively.

15 4-[Trans-4-(trans-4-propylcyclohexyl)cyclohexyl]-  
2-fluoroacetophenone of Example 3 (10 parts by weight)  
was added to the above liquid crystal composition (B)  
(90 parts by weight). The resulting liquid crystal  
composition exhibited a N-I point of 62°C, and  
20 its viscosity at 20°C was 24 cp. i.e. almost unchanged.

Thus, when the compound of the present invention was added, it was possible to obtain a liquid crystal composition having a low viscosity and a high clearing point.

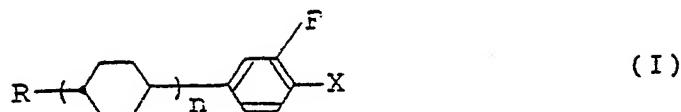
Use example 4

A liquid crystal composition consisting of the above liquid crystal composition (B) (90 parts by weight) and 3-fluoro-4-cyano-1-[trans-4-(trans-4-propylcyclohexyl)-5-cyclohexyl]benzene of Example 4 (10 parts by weight) had a N-I point of 66°C and a  $\Delta\epsilon$  of +12.5, and when a TN cell was prepared in the same manner as above, the threshold voltage and the saturation voltage lowered down to 1.40 V and 1.90 V, respectively, and the viscosity increased up to 29 cp, but such an extent of value is not practically a hindrance.

As described above, when the compound of the present invention is used, it is possible to reduce the operation voltage of display elements and also to 15 broaden their operation temperature range.

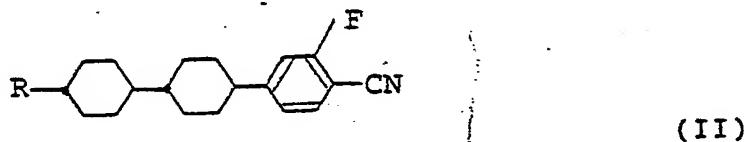
## CLAIMS

1. A flurobenzene derivative expressed by the general formula



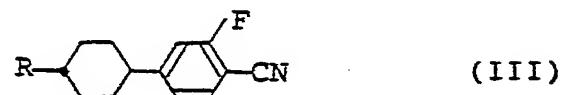
5 wherein n represents 1 or 2, X represents CN or COCH<sub>3</sub> and R represents a hydrogen atom or an alkyl or alkoxy group of 1 to 15 carbon atoms.

2. A 3-fluoro-4-cyano-1-[trans-4-(trans-4-substituted cyclohexyl)cyclohexyl]benzene expressed by the general  
10 formula



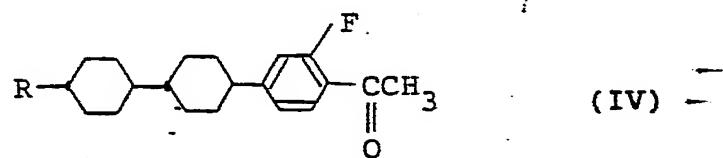
wherein R represents a hydrogen atom or an alkyl or alkoxy group of 1 to 15 carbon atoms.

3. A 3-fluoro-4-cyano-1-(trans-4-substituted cyclohexyl)benzene expressed by the general formula



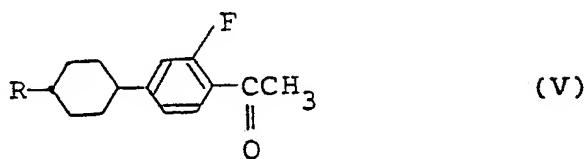
wherein R represents an alkyl or alkoxy group of 1 to 15  
5 carbon atoms.

4. A 4-[trans-4-(trans-4-substituted cyclohexyl)-cyclohexyl]acetophenone expressed by the general formula



wherein R represents an alkyl or alkoxy group of 1 to 10  
10 carbon atoms.

5. A 4-(trans-4-substituted cyclohexyl)acetophenone  
expressed by the general formula



wherein R represents an alkyl or alkoxy group of 1 to 10  
5 carbon atoms.

6. A liquid crystal composition containing at least one  
fluorobenzene derivative as defined in any preceding  
claim.

7. A process for preparing a compound of formula (I).  
10 as defined in claim 1, wherein a 1-fluoro-3-  
(4-substituted cyclohexyl)benzene corresponding to a  
compound of formula (I) which has hydrogen in place of  
the substituent X, is acetylated to give a compound of  
formula (I) where X is COCH<sub>3</sub>, and the COCH<sub>3</sub> group is  
15 optionally converted to a nitrile group.



DOCUMENTS CONSIDERED TO BE RELEVANT			EP 84301072.9
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
P, X	EP - A1 - 0 090 183 (MERCK PATENT GESELLSCHAFT MIT BESCHRÄNKTER HAFTUNG * Claims 1,4 *---	1-6	C 07 C 121/60 C 07 C 121/75 C 07 C 120/00 C 07 C 49/813 C 07 C 49/84 C 07 C 45/46 C 09 K 3/34
A	DE - A1 - 3 223 637 (CHISSO CORP.) * Claims 1,4; pages 8,9 *---	1-3,6, 7	
A	DE - A1 - 2 918 775 (MERCK PATENT GMBH) * Claims 1,2,7,8 *---	1,5,6	
A	GB - A - 2 090 593 (HOFFMANN - LA ROCHE & CO. AKTIENGESELLSCHAFT) * Claims 1,14,15 *----	1,4,6, 7	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			C 07 C 49/00 C 07 C 121/00 C 09 K 3/00
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
VIENNA	23-05-1984	HOFBAUER	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone		T : theory or principle underlying the invention	
Y : particularly relevant if combined with another document of the same category		E : earlier patent document, but published on, or after the filing date	
A : technological background		D : document cited in the application	
O : non-written disclosure		L : document cited for other reasons	
P : intermediate document		& : member of the same patent family, corresponding document	